

# CrO<sub>2</sub>: a self-doped double exchange ferromagnet

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Band structure calculations of CrO<sub>2</sub> carried out in the LSDA+U approach reveal a clear picture of the physics behind the metallic ferromagnetic properties. Arguments are presented that the metallic ferromagnetic oxide CrO<sub>2</sub> belongs to a class of materials in which magnetic ordering exists due to double exchange (in this respect CrO<sub>2</sub> turns out to be similar to the CMR manganates). It is concluded that CrO<sub>2</sub> has a small or even negative charge transfer gap which can result in self-doping. Certain experiments to check the proposed picture are suggested.

75.50.Ss, 71.20.-b, 75.30.Et

There has been a revival in interest in 3d transition metal oxides during the last decade. This was initially stimulated by the discovery of High-T<sub>c</sub> superconductivity in complex copper oxides, and more recently by the active study of the colossal magnetoresistance manganates (CMR) La<sub>1-x</sub>(Ca,Sr)<sub>x</sub>MnO<sub>3</sub>. These latter systems in the most interesting composition range are metallic ferromagnets. This is interesting in itself because ferromagnetic ordering is rare among the oxides: most of them are antiferromagnetic or ferrimagnetic with dominating antiferromagnetic interactions. We need to meet certain special conditions to stabilize ferromagnetism. One of the main mechanisms invoked to explain ferromagnetic ordering in these systems is the double exchange mechanism [1], although it is not the only one [2].

Another very well known ferromagnetic and metallic compound is chromium dioxide CrO<sub>2</sub> widely used in magnetic recording tapes. In its formal 4+ valence state Cr has two 3d electrons in t<sub>2g</sub> orbitals which in a simple picture of strong correlations would suggest a Mott insulating-like ground state with S=1 local moments and most likely antiferromagnetic spin order. This seems to be about as far from the actual observed properties as one can get. In this letter we will address this problem using band structure methods supplemented with local Coulomb and exchange interactions (LSDA+U, [3]) interpreted in terms of local electronic configurations. We will argue that the d electrons can be divided into a localized "core" of spin ½ and an itinerant d electron propagating through these "cores" resulting in a double exchange-like mechanism for the ferromagnetic order much as in the manganates. We also show that strong electron correlation effects do not in this case lead to an insulating ground state for reasonable values of the d-d Coulomb interaction and perfect stoichiometry because CrO<sub>2</sub> should be viewed as a small or even negative charge transfer gap [4] material in the Zaanen-Sawatzky-Allen (ZSA) scheme

[5] quite unlike the parent CMR material LaMnO<sub>3</sub> which is a Mott-Hubbard insulator. This leads for CrO<sub>2</sub> quite naturally to a phenomenon which could be referred to as self-doping resulting in a non-integral 3d band occupation [6].

CrO<sub>2</sub> is a ferromagnetic metal with a saturation magnetic moment of 2.00 μ<sub>B</sub> and a low temperature resistivity with a nearly T<sup>2</sup> temperature dependence [7]. Band structure calculations in LSDA [8] explain this behaviour as that of a half-metallic ferromagnet with a gap in the minority spin band resulting in the integral magnetic moment per formula unit in spite of the strong covalency effects. However the magnetic susceptibility in the paramagnetic phase exhibits a Curie-Weiss-like behaviour with a local moment of also 2 μ<sub>B</sub> indicating that the mechanism for ferromagnetic behaviour is not a band (Stoner-like) mechanism. Local moments indicate strong correlation effects and this was in fact suggested by early photoemission data [9] which looked more like those of a semiconductor with a vanishing density of states (DOS) at the Fermi energy and a spin polarization of nearly 100 % for binding energies about 2 eV below the Fermi level. To resolve this controversy we carried out the calculations in the LSDA+U approach which is superior to LSDA since it can indeed yield a gap if the local Coulomb interactions are large enough.

CrO<sub>2</sub> has a rutile structure (space group D<sub>4h</sub><sup>14</sup>: P4<sub>2</sub>/mnm) in which the unit cell consists of two formula units. The Bravais lattice is tetragonal (c/a=0.65958) with a lattice constant of a=4.421 Å [10]. The Cr atoms form a body-centered tetragonal lattice and are surrounded by distorted oxygen octahedra. The octahedra surrounding Cr at the body's center and corner positions differ by a 90° rotation about the c axis (see also Fig.1 where Cr1 and Cr2 atoms are in the corners of the unit cell and Cr3 atom is in the body center position).

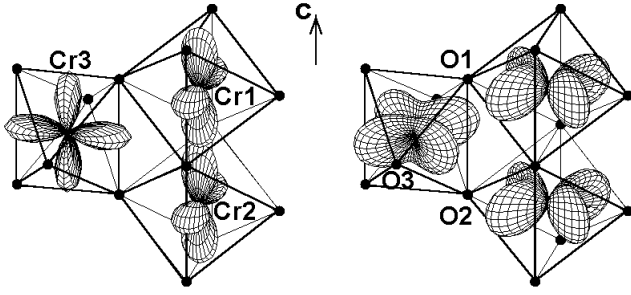


FIG. 1. Angular distribution of  $xy$  (left) and  $(yz + zx)$  (right) electron spin density for the nearest Cr neighbors. Direction of crystallographic  $c$ -axis is shown by arrow. Solid circles denote oxygen atoms.

The simplest  $\text{CrO}_6$  cluster calculations showed, that this kind of distortion of the octahedra (elongation along  $c$  axis) leads to the new natural basis for the  $t_{2g}$  orbitals:  $xy$ ,  $(yz + zx)$  and  $(yz - zx)$  in a local coordinate system (LCS) for every octahedron. In this LCS the  $z$ -axis is directed to the apex oxygen and the  $x$  and  $y$  axes – to the basal plane oxygens. Again referring to the Fig.1, in which for Cr3 atom  $z$ -axis is directed to the O3 oxygen and  $x$ ,  $y$  axes – to the O1 and O2 oxygens. At the same time, the O1 and O2 become apex oxygens for Cr1 and Cr2, and  $z$  axis is directed to these oxygens there. We will demonstrate below that this distorted structure is responsible for rather peculiar properties of the  $d$  bands.

LSDA+U calculations were performed in the linearized muffin-tin orbitals (LMTO) approach [11] with atomic spheres radii of 2.06 a.u. for Cr and 1.78 and 1.62 a.u. for the two kinds of empty spheres used (8 per unit cell in total) to fill the empty space as much as possible. The spherical harmonics were expanded to the value of  $l_{max}=3$  and 2 for the atomic and empty spheres, respectively. For the Brillouin zone (BZ) integration 1300  $\mathbf{k}$ -points were used. The screened  $U$  and  $J$  parameters used in the LSDA+U scheme were calculated by constrain method taking into account participation

of  $e_g$  electrons in screening of the  $t_{2g}$  electrons [12] and found to be 3 and 0.87 eV, respectively.

The results of this calculation are shown in Figs. 2-4. First, for  $U=3$  eV the material is found to be a half-metallic ferromagnet, similar to the previous LSDA results [8]. However, inclusion of the electron correlations modifies the electronic structure. Together with the shift of the minority spin DOS from the bottom of the conduction band to higher energy, there appears a dip in the majority spin DOS at the Fermi level which can be taken as an indication of the tendency toward a gap formation. The decrease of the DOS at  $E_F$  in comparison with that obtained in [8] may be partially responsible for the reduced signal close to  $E_F$  observed in photo-electron spectroscopy [9]. In our calculations, however,  $\text{CrO}_2$  is still a metal albeit with the reduced DOS at the Fermi level. An explanation of this discrepancy may lie, e.g., in the modified situation at the surface. Note also that more recent photoemission data [13] show a finite DOS at  $E_F$ , and the spectrum obtained in [13] is in rather good agreement with our calculations.

The tendency to open a gap in an energy spectrum which we noticed above was confirmed by calculation with larger values of  $U$ . It was found that the gap would indeed open at  $U \geq 6$  eV which would make  $\text{CrO}_2$  a Mott-Hubbard insulator.

There are other aspects of the calculation that are very interesting and may provide the clues to the basic mechanism for the ferromagnetic metal behaviour. First notice the almost dispersionless majority spin band at about 1 eV below  $E_F$  in Fig.2 over a large region of the BZ which as is indicated by the black circles has almost pure  $d$  character. This is observed as a peak in the DOS in Figs.3 and 4, and corresponds to strongly localized  $xy$  orbitals completely occupied by one majority spin electron. Because these states have almost pure  $d$  character they are very sensitive to the size of  $U$  and shift further away from  $E_F$  as  $U$  increases.

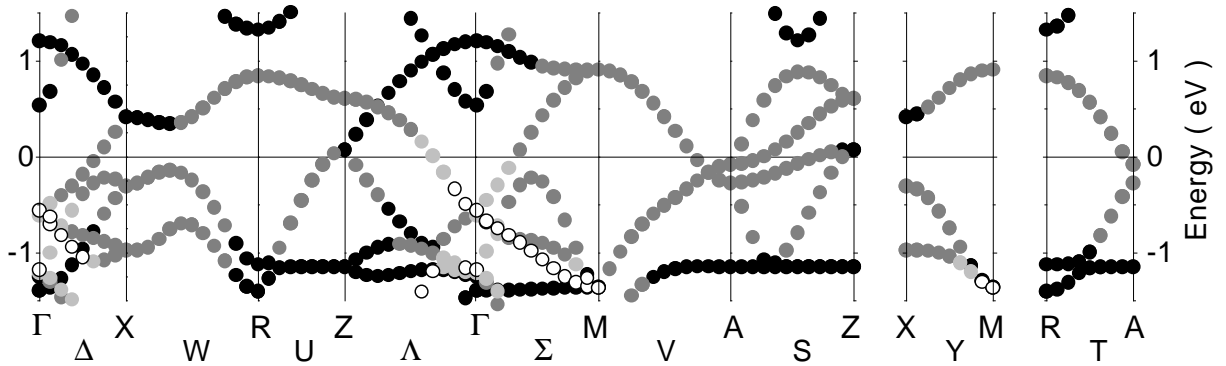


FIG. 2. LSDA+U band structure of  $\text{CrO}_2$  for majority spin-sublattice in the vicinity of the Fermi level. Open circles denote the contribution of  $d$  states less than 25 %, light gray circles – between 25 and 50 %, gray – between 50 and 75 %, and black – predominantly  $d$  character of the band. Fermi level is denoted by horizontal solid line.

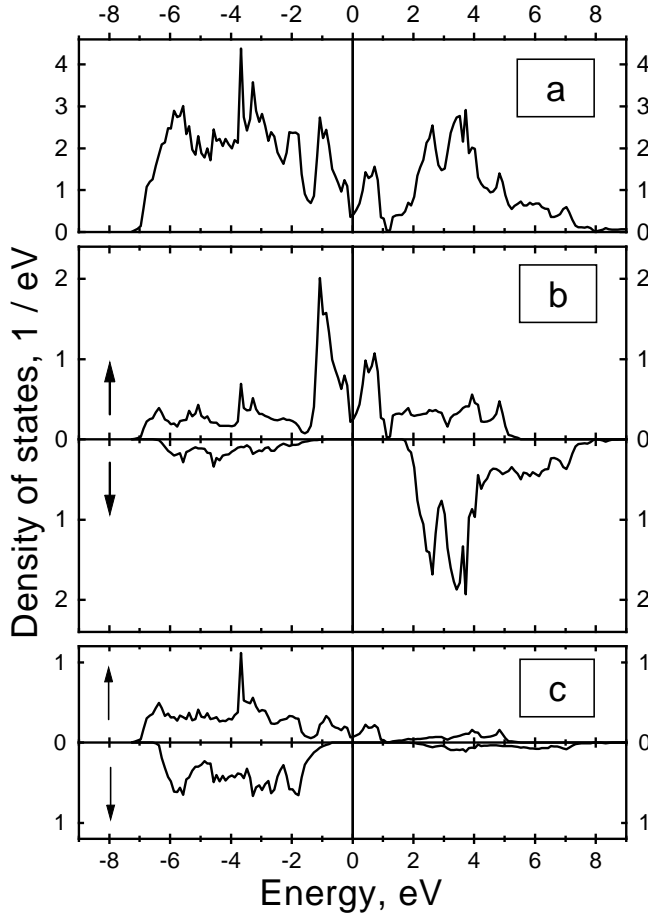


FIG. 3. Total (per formula unit and both spins, a) and partial Cr 3d- (b) and O 2p- (c) density of states of CrO<sub>2</sub>.

The other  $t_{2g}$   $d$ -bands are strongly hybridized with O and form dispersive bands crossing the Fermi level. One can see from Fig.4 that predominantly the  $(yz + zx)$  is occupied at each site, see also Fig.1. An admixture of oxygen states strongly softens the influence of  $U$  on these bands and that is the reason that such a high value of  $U=6$  eV is required for a gap to open in these bands. This indicates that we are dealing with a system of localized  $S=\frac{1}{2}$   $xy$  electrons exchange coupled to broader band-like and strongly hybridized  $(yz + zx)$  states. In our case the bandwidth of  $d$ - $p$   $\pi$ -bands is comparable with the Hund's rule intraatomic exchange ( $\sim 1$  eV). This is reminiscent of a double exchange ferromagnetic mechanism of Zener [1]. This is also consistent with the half-metallic nature of this material. Thus, the (half-)metallic character and ferromagnetism are indeed closely connected.

An extra confirmation of this conclusion came from the calculation, in which we artificially imposed an antiferromagnetic ordering. The simplest two-sublattice antiferromagnetic structure was chosen, with the spin in the body center sites opposite to the spins at the corners of the unit cell. The band structure obtained has a small gap  $\sim 0.15$  eV exactly at the Fermi-surface. That means

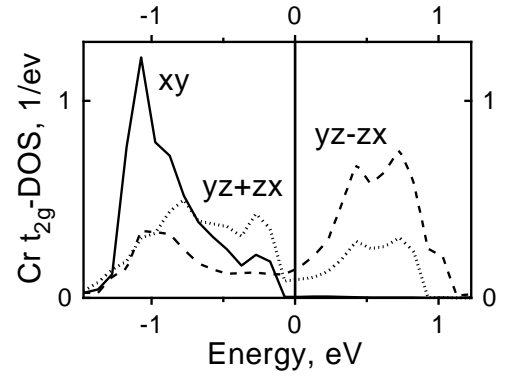


FIG. 4. Partial Cr  $t_{2g}$  majority spin density of states in the vicinity of the Fermi level.

that CrO<sub>2</sub> in an antiferromagnetic phase would have been an insulator. Thus, the metallicity and ferromagnetism in CrO<sub>2</sub> do indeed support each other, which is in full agreement with the double exchange picture.

The reason for this dualistic behaviour of the  $t_{2g}$  states i.e some localized and others dispersive, can be found in the distortion from an ideal rutile-type crystal structure [14]. Our calculations show that in the ideal structure with the same length of all 12 O-O bonds in a perfect oxygen octahedron, all the  $t_{2g}$  bands would have the same width. In the real distorted structure the edge sharing nearest Cr neighbors (Cr1 and Cr2 in Fig.1) move apart decreasing the  $xy$  bandwidth and shifting its center of gravity to low energies in comparison with the centers of gravity of the other two  $t_{2g}$  bands. And now with the inclusion of Coulomb interactions, this  $xy$  band becomes the first candidate to be fully occupied. Just that happened in our LSDA+ $U$  calculation. This picture has much in common with the band structure, proposed by Goodenough [15] on phenomenological grounds.

It is possible to visualize the  $d$  orbitals mentioned above (in particular, occupied orbitals) by plotting the angular distribution of  $d$  electron spin density for these orbitals (Fig.1):

$$\rho(\theta, \phi) = \sum_{m, m'} Q_{m, m'} Y_m(\theta, \phi) Y_{m'}^*(\theta, \phi) \quad (1)$$

where  $Q_{m, m'} = n_{m, m'}^{\uparrow} - n_{m, m'}^{\downarrow}$  is the  $d$  spin occupation number for the case of  $xy$  orbital or  $2 \times 2$  matrix for the case of  $(yz + zx)$  orbital obtained in our self-consistent calculation and  $Y_m(\theta, \phi)$  are corresponding spherical harmonics. Note that  $(yz + zx)$  orbitals of Cr atoms hybridize with each other via  $\pi$ -overlap with O1 and O2 oxygens (right panel of Fig.1).

Yet another interesting feature is that there are bands of predominantly O 2p character crossing the Fermi level close to the  $\Gamma$ -point (Fig.2). The absence of hybridization of these with the  $d$  states indicates that they have symmetries such that this mixing is not allowed. The fact that they extend to the Fermi level is important. This means that these states can be used as electron or

hole reservoirs causing a non-integral occupation of the  $d$  bands. This may be called self-doping. This again is a reason for the metallic behaviour in spite of quite large  $U$  values.

The situation when the almost pure O  $2p$  bands cross the Fermi level indicates that such materials should be considered as lying in the small or even negative charge transfer gap region of the ZSA diagram. The negative charge transfer gap behaviour is not unexpected for oxides with transition metals in very high oxidation states because of the increased electron affinity of these ions. This conclusion can in principle be checked by the  $1s-2p$  x-ray absorption on oxygen; simultaneously certain spin polarization should be transferred to oxygen which would be very interesting to study experimentally. In our calculations the oxygen polarization turned out to be opposite to the polarization of  $d$ -ions and equal to  $-0.09 \mu_B$  per oxygen.

One more conclusion of the picture obtained is that, as is common for the double exchange systems, one should expect a negative magnetoresistance in the paramagnetic region. Previous results have shown that the magnetoresistance of  $\text{CrO}_2$  is rather small [7,16], but these measurements were done only below room temperature. It would be interesting to extend these measurements to the region of  $T > T_c = 392$  K. As there is no extra "complications" in  $\text{CrO}_2$  as compared to CMR manganates (no strong Jahn-Teller effects, no disorder, no formally different valence ions), this study would reveal a pure double exchange contribution to magnetoresistance which, when compared with similar data for manganates, could help to discriminate between the contribution of different mechanisms in the latter.

Summarizing, we carried out an extensive band structure calculations of  $\text{CrO}_2$  in the LSDA+ $U$  approach. We confirmed the half-metallic nature of  $\text{CrO}_2$ , albeit with the dip of DOS at the Fermi level. It is demonstrated that there exist in  $\text{CrO}_2$  two groups of  $d$ -electrons with significantly different properties: one of the two  $d$ -electrons of  $\text{Cr}^{4+}$  is essentially localized, and another is  $\pi$ -bonded with the oxygen  $p$ -orbitals and forms a partially filled narrow band. The width of this band is of the same order as the Hund's rule intraatomic exchange interaction. The resulting picture may be interpreted as an indication that the ferromagnetism in  $\text{CrO}_2$  is due to double exchange mechanism. An extra confirmation of this conclusion comes from the fact that in an antiferromagnetic phase  $\text{CrO}_2$  would have been an insulator. The strong contribution of the oxygen  $p$ -states at the Fermi surface

explains why this material is not a Mott insulator in spite of the large  $U$  values and the relatively narrow  $d$ -bands and also shows that  $\text{CrO}_2$  belongs to the class of compounds with small or even negative charge-transfer gap leading to a self-doping. Several experiments are suggested which could check the proposed picture and could help to isolate the double exchange contribution to magnetoresistance.

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